

CHAPTER 4

Trace Elements: Heavy Metals and Micronutrients

INTRODUCTION

Trace elements are required in small amounts by plants or animals. Some of these have been identified while others may still be unknown. Heavy metals are a group of elements found in the periodic table with a relatively high molecular weight (density $>5.0 \text{ mg/m}^3$) and, when taken into the body, can accumulate in specific body organs. Ashworth (1991) argues that the term “heavy metals” is a misnomer, because at least two elements, arsenic and selenium, are not metals. The trace elements often referred to as heavy metals that have been regulated are: arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn). Chromium (Cr) was regulated in the first draft of the 503 regulations issued in 1993. In 1995, Cr was deleted.

In this chapter, the term *trace elements* will be used except where the literature specifically uses the term *heavy metals*.

Micronutrients are those essential trace elements that are needed in relatively small quantities for growth of plants, animals, or humans. The eight plant micronutrients are: boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) (Mortvedt et al., 1991). Elements such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg) are referred to as macronutrients because they are required in large amounts by plants. The elements cobalt (Co), iodine (I), Cu, Fe, Mn, Mo, Se and Zn are trace elements essential for animal nutrition (Miller et al., 1991).

Several other elements — arsenic, boron, bromine, cadmium, lithium, nickel, lead, silicon, tin and vanadium — have more recently been proposed as essential to some animal species (Van Campen, 1991). Van Campen identifies eight essential trace elements for human nutrition: Cu, Cr, Fe, I, Mn, Mo, Se and Zn.

The heavy metals indicated in the USEPA and state regulations are trace elements that can be harmful to the environment, humans, animals and plants. Consequently, both regulations and literature rarely consider whether these elements are also essential to humans, animals, or plants. At many agricultural areas in the United

Table 4.1 Trace Metal Content of Yard Waste

Heavy Metal	Number of Samples	Mean mg/kg	SD	Min. mg/kg	Max. mg/kg	CV
Arsenic	5	4.8	5.05	1	12.8	106.16
Boron	30	28.7	17.93	0.2	76	62.41
Cadmium	29	0.32	0.20	0.04	0.81	62.22
Chromium	35	39.4	45.41	3.7	236	115.39
Copper	35	64	65.47	8	327	102.15
Lead	35	69.6	54.49	11.4	235	78.34
Mercury	22	0.19	0.11	0.04	0.5	59.57
Molybdenum	17	0.22	0.32	0.05	1.09	143.59
Nickel	33	26.89	28.27	3.27	152	105.13
Selenium	17	0.33	0.10	0.1	0.55	31.89
Zinc	35	153.0	74.13	41.6	295	48.47

Source: Epstein, 1997, *The Science of Composting*, Technomic, Lancaster, PA. With permission.

States, farmers apply small quantities of a trace element, which is also regulated as a heavy metal. Horticulturalists often add trace elements needed for plant nutrition even though several are considered heavy metals by regulators.

Biosolids contain trace elements as a result of atmospheric deposition on land, natural vegetation, food sources (because plant material will contain trace elements), industrial sources, fertilizers and pesticides, human wastes (due to ingestion of food and water) and natural soil. All of these materials can find their way into the sewer system and eventually end in the wastewater treatment plant and into biosolids. As an example, Table 4.1 shows the concentration of trace elements in yard waste.

The subject of trace elements in biosolids and their impact on human health and the environment has been very extensively studied over the past 30 years. Two chapters are devoted to this subject. This chapter covers environmental aspects and human health, while Chapter 5 discusses soil–plant interactions.

The objectives of these chapters are to:

- Provide data on the sources of trace elements, heavy metals and micronutrients in the environment
- Discuss the toxicology of trace elements
- Discuss the fate of trace elements in soils as they relate to plant uptake and the environment
- Provide information on uptake of trace elements by plants.

SOURCES OF TRACE ELEMENTS, HEAVY METALS, AND MICRONUTRIENTS IN THE ENVIRONMENT

Soils are derived from parent material as a result of weathering. Because many of the parent material minerals contain trace elements, natural soils will contain different amounts of trace elements depending on the type of mineral. Krauskopf (1967) reported that shale contained 6.6 mg/kg As; 0.3 mg/kg Cd; 57 mg/kg Cu; 20

Table 4.2 Trace Elements in Natural Soils, Agricultural Soils and Fertilizers in the United States

Element	Range in Natural Soil ¹ mg/kg	Range in Agricultural Soils ² mg/kg	Range in Fertilizers ³ mg/kg
Arsenic	5–13	NA	0.3–1662.3
Cadmium	0.01–7	<0.0010–2.0	0.75–398
Chromium	23–15,000	NA	1.3–338.9
Copper	1–300	<0.6–495	1.0–29,650
Lead	2.6–25	<1.0–135	4.6–10,013
Mercury	NA	NA	0.011–3.36
Nickel	3–300	0.7–269	1.4–890
Selenium	0.0001–3.4	NA	NA
Zinc	10–2,000	<3.0–264	1.6–77,300

¹ Based on Conner and Shacklett, 1975

² Holmgren et al., 1993

³ Moss et al., 2002

NA – not available

mg/kg Pb; and 80 mg/kg Zn. The values for granite were 1.5 mg/kg As; 0.2 mg/kg Cd; 10 mg/kg Cu; 20 mg/kg Pb; and 40 mg/kg Zn.

In Minnesota, soils developed from lacustrine clays (formed in lakes) have a higher level of Cd than other soils (Pierce et al., 1982). Arsenic occurs in more than 200 naturally occurring minerals (Onken, 1995). One of the major agricultural production areas in California, Salinas Valley, contains high levels of Cd due to a natural geological source: the Monterey shale. Cadmium concentrations in the surface soils ranged from 1.4 to 22 µg/g with an average 8.0 µg/g (Lund et al., 1981).

Many agricultural soils may have higher levels of heavy metals than normally found in natural soils as the result of atmospheric deposition and application of fertilizers, pesticides and biosolids. Haygarth et al. (1995) reported that from 30% to 53% of Se found on pasture leaves resulted from atmospheric deposition. Several other researchers have reported on significant deposition of Pb, Cd, As, Cu and Zn (Haygarth et al., 1995; Hovmand et al., 1983; Berthelsen et al., 1995; Harrison and Chirgawi, 1989).

Mortveldt et al. (1981) reported on the uptake of Cd by wheat from phosphorus fertilizers. Lee and Keeney (1975) found that the application of fertilizers added more Cd and Zn to soils in Wisconsin than biosolids at that time. Table 4.2 shows the heavy metal content of natural soils, agricultural soils and fertilizers (Conner and Shacklett, 1975; Holmgren et al., 1993). Mermut et al. (1996) reported that phosphate fertilizers can be a significant source of trace elements and suggested that some of these elements, especially Cd, Cr and Zn, can be a source of soil pollution.

In 1997, Washington State published a survey on heavy metals in fertilizers and industrial by-product fertilizers (Bowhay, 1997). Table 4.3 summarizes some of the data. Although the level of many heavy metals and other trace elements can be low in agricultural fertilizers, repeated applications over long periods of time could result in significant uptake and accumulation by food crops.

Table 4.3 Concentration of Heavy Metals in Some Fertilizers and Industrial By-Product Fertilizers

Element	Number of Samples Detected	Range in Concentration mg/kg
Arsenic	36	4.2–1,040
Cadmium	12	0.63–275
Copper	36	0.094–39,900
Lead	11	2.5–11,300
Mercury	36	0.006–3.36
Molybdenum	14	1.3–17.8
Nickel	16	1.5–195
Selenium	36	Not detected
Zinc	36	0.21–203,000

Source: Adapted from Bowhay, 1997.

Arsenic has been used as a defoliant for several crops prior to the 1980s and is still used in cotton. Blueberry and potato soils in Maine, where arsenic has been used as a defoliant, showed an increase in the level of this element. Lead arsenate and calcium arsenate previously have been used in cotton and orchards (Woolson et al., 1971). Many urban soils contain high levels of Pb as a result of lead-based gasoline or paints. Because Pb does not move readily through the soil, high levels will remain in surface soils for many years. Holmgren et al. (1993) analyzed 3,045 surface soil samples throughout the United States. Table 4.4 shows a summary of the data. Holmgren et al. found regional as well as local differences due to soil parameters. Soil Cd was lower in the southeast and generally higher in California, Michigan and New York. Organic soils had higher amounts that might have been the result of heavy application of phosphate fertilizers used in intensive vegetable production.

Low levels of Pb were found in the southeast. Some areas in Virginia and West Virginia had levels exceeding 3000 mg/kg. High levels of Pb were also found in the Ohio, Mississippi and Missouri River valleys. Some have suggested that the high levels may have been a result of industrial contamination.

Zinc levels were low in the southeast with moderately high levels in California, the southwest, Colorado and the lower Mississippi valley. Copper levels were also lower in the southeast with the exception of Florida. High levels were found in organic soils used for vegetable production in Florida, Michigan and New York, presumably as a result of fertilizer applications to correct Cu deficiency. Ma et al. (1997) reported much lower metal contents in 40 mineral soils of Florida. Organic soils had considerably higher levels of heavy metals than mineral soils. The higher the clay content, the higher the metal concentration.

Dudas and Pawluk (1980) determined the background levels of As, Cd, Co, Cu, Pb and Zn in Chernozemic and Luvisolic soils from Alberta, Canada. Arsenic ranged

Table 4.4 Geometric Means for Some Heavy Metals in U.S. Agricultural Surface Soils by Soil Texture

Soil Texture	Number of Samples	Cd	Zn	Cu	Ni	Pb
mg/kg Dry Soil						
Loamy sand	384	0.055 g*	14.9 f	6.0 h	6.2 h	5.5 h
Sandy loam	208	0.096 f	26.1 e	10.8 g	11.6 fg	8.3 f
Fine sandy loam	308	0.107 f	28.3 e	10.3 g	12.1 fg	7.3 g
Silt	745	0.185 e	50.4 d	18.1 f	12.4 d	13.4 g
Loam	326	0.199 e	48.4 d	18.6 f	20.6 e	10.6 e
Silty clay loam	322	0.288 d	76.9 b	28.7 d	35.5 c	16.0 c
Clay	108	0.289 d	98.0 a	37.6 c	52.0 a	17.7 ab
Clay loam	148	0.294 d	65.3 c	22.7 e	28.4 d	12.1 d
Silty clay	59	0.388 c	97.7 a	33.6 c	43.1 b	16.4 bc
Muck	190	0.558 b	65.3 c	75.8 b	11.2 g	10.9 c
SAPRIC	88	0.811 a	59.7 c	97.9 a	12.8 f	18.3 a
All	2886	0.178	43.2	18.3	16.9	10.5

* Means within a column followed by the same letter are not statistically significant.

Source: Holmgren et al., 1993, *J. Environ. Qual.* 22: 335–348. With permission.

from 0.82 to 6.9 mg/kg; Cd from 0.53 to 0.6 mg/kg; Co from 6.4 to 15 mg/kg; Cu from 11 to 49 mg/kg; Pb from 15 to 41 mg/kg; and Zn from 29 to 235 mg/kg. Cd and Zn levels in Canadian soils were higher than those reported by Holmgren et al. (1993) for U.S. agricultural soils.

It is very evident from these data that trace elements, including heavy metals, are found universally in our environment.

TRACE ELEMENTS IN BIOSOLIDS

Biosolids contain trace elements and heavy metals primarily from industrial, commercial and residential discharges into the wastewater system. As a result of the Clean Water Act of 1972 restricting industrial discharge, the quality of the wastewater entering publicly owned treatment works (POTW) systems has improved. Consequently, the quality of biosolids has improved. Changes in materials used in domestic residences have also affected wastewater quality. Lead was used in early plumbing and is now prohibited. To a large extent, plastic piping has replaced copper piping.

Table 4.5 compares the heavy metals from an early 40-city POTW study conducted in 1979–80 to the 1988–89 National Sewage Sludge Survey (NSSS). Technically the data are not comparable. However Cd, Cr, Pb and Ni were greatly reduced. There was little change in Zn and Cu (USEPA, 1990). A comparison between U.S. and Canadian heavy metal concentrations is shown in Table 4.6 (based on a report prepared for the Water Environment Association of Ontario, 2001).

Industrial pretreatment in many of the large cities resulted in major reductions in heavy metals.

Table 4.5 A Comparison of Heavy Metal Concentrations in 40 POTWs in 1980 to the NSSS Study in 1988

Element	Samples	Percent Detected	Mean mg/kg	SD	Coefficient of Variation
Arsenic	199	80	9.9	18.8	1.9
	45	100	6.7	6.59	0.98
Cadmium	198	69	6.94	11.8	1.69
	45	100	69.0	252	3.65
Chromium	199	91	119	339.2	2.86
	45	100	429	440.8	1.03
Copper	199	100	741	961.8	1.30
	45	100	602	528.8	0.88
Lead	199	80	134.4	197.8	1.47
	45	100	369	331.5	0.90
Mercury	199	63	5.2	15.5	2.98
	45	100	2.8	2.6	0.93
Molybdenum	199	53	9.2	16.6	1.79
	45	75	17.7	16.7	0.94
Nickel	199	66	42.7	94.8	2.22
	45	100	135.1	169.1	1.25
Selenium	199	65	5.2	7.3	1.42
	45	100	7.3	29.10	4.16
Zinc	199	100	1,202	1,554.4	1.29
	45	100	1,594	1,759.3	1.10

Source: USEPA, 1990.

Table 4.6 Comparison of Heavy Metal Concentration in United States and Canadian Biosolids

Element	United States Surveys mg/kg Dry Weight			Canadian Surveys mg/kg Dry Weight	
	1979	1988	1996	1981	1995
Arsenic	6.7	9.9	11.5		2.3
Cadmium	69	6.9	6.4	35	6.3
Chromium	429	119	103	1,040	319
Copper	602	741	506	870	638
Lead	369	134	111	545	124
Mercury	2.8	5.2	2.1		3.5
Molybdenum	17.7	9.2	15		22
Nickel	135	43	57	160	38
Selenium	7.3	5.2	5.7		3.3
Zinc	1594	1202	830	1,390	823

Sources: Webber and Nichols, 1995; Lue-Hing et al., 1999.

TRACE ELEMENTS IN ANIMALS, HUMANS, SOILS, AND PLANTS

Arsenic (As)

Animals and Humans

Arsenic is toxic to animals and man. The maximum tolerable levels of dietary inorganic As is 50 mg/kg for cattle, sheep, swine, poultry, horse and rabbit. The tolerable level of organic As is 100 mg/kg for the same animals (NRC, 1980). Under natural dietary conditions, As toxicity is uncommon (Gough et al., 1979). There have been reports on cattle and sheep toxicity from grazing on pastures containing high levels of As in soils treated with arsenicals (Selby et al., 1974; Case, 1974). Arsenic bioavailability has been shown to be five times less available than As from the salt Na_2HAsO_4 .

Arsenic is believed to be essential to mammals (Chaney, 1983). Several organic arsenic compounds have been fed to pigs and poultry to stimulate growth (Gough et al., 1979). The data cited above indicate that the potential for As toxicity to human and animal food chain from land applied biosolids is very minimal for the following reasons:

- Levels of As in biosolids are very low.
- Arsenic in biosolids is in an organic matrix and is less available than salts; bioavailability of As from an organic matrix is very low.
- The food chain is protected because As phytotoxicity will affect crops consumed by humans and animals.
- Arsenic is not readily taken up by plants.

Soils

The two most common inorganic forms of As in soils are arsenate and arsenite. Arsenic under aerobic conditions in the soil reverts to the chemical form of arsenate, which is strongly bound to the clay fraction. This binding reduces the potential of As to migrate through soils and inhibits its uptake by plants. Arsenite is formed under anaerobic conditions and is more phytotoxic. It is not adsorbed on soil particles to as great extent as arsenate. Consequently, more As is in the soil solution and can cause phytotoxicity (Tsutsumi, 1981; Chaney and Ryan, 1994). In flooded soils arsenite will predominate. Phosphate will displace adsorbed As which allows it to leach down and be readsorbed at lower levels (Onken and Hossner, 1995).

Plants

Arsenic is not considered essential to plants and is not readily taken up by plants. It tends to accumulate in the roots, which reduces its concentration in edible above-ground portions of plants (U.S. Department of Agriculture, 1968).

Arsenic can be toxic to plants. The toxicity is a function of the concentration of the soluble, not total, arsenic content of soils (Gough et al., 1979). Toxicity to As

has been primarily related to the use of pesticides (Chaney, 1983; Gough et al., 1979). Calcium arsenate, lead arsenate and cupric arsenate (Paris green) were widely used as insecticides (Gough et al., 1979). The use of As insecticides in orchards has resulted in high levels of soluble As, rendering the soils of some orchards unproductive (Gough et al., 1979).

Arsenicals have been used as defoliants in cotton and potatoes (Woolson, 1983). Wells and Gilmore (1977) reported that phytotoxicity to rice occurred when cotton fields were used for rice production. Rice grown in flooded soils is the most sensitive crop to As toxicity from soil As. High concentrations of soil As can be phytotoxic to many crops including peas, potatoes, cotton and soybeans (Stevens et al., 1972; Deuel and Swoboda, 1972). Deuel and Swoboda reported that 4.4 $\mu\text{g/g}$ or greater As concentration in cotton and 1 $\mu\text{g/g}$ and greater in soybeans limited yield. Under flooded conditions, the rate of As uptake by rice increased as the rate of plant growth increased.

Jacobs et al. (1970) showed that As residues in soils from potato cultivation, where Na-arsenite was used as a defoliant, decreased yields of vegetables. Stevens et al. (1972) reported that on As contaminated sand, arsenic levels were contained in the potato peel with very low amounts in the tuber.

Most of the data on As toxicity to plants are from the use of salts and not from As in biosolids or other organic matrices. As is phytotoxic before crops can accumulate As to a level which is toxic to humans. Therefore, the food chain is protected (Chaney, 1983).

Cadmium (Cd)

In addition to being a natural element in soils and geological material, Cd enters our environment from fertilizers, phosphatic materials, zinc-associated compounds, plastics, batteries, land application wastes or waste products, coated metals, paints and smelting and purification of metal ores. Many of the world's agricultural areas are contaminated to some extent with Cd. The use of biosolids could further add to the soil burden.

How significantly could the addition of Cd, through the application of biosolids, impact the food chain and how might this affect the health of animals and humans? The answer to this question depends on numerous factors, including uptake and accumulation by plants and their organs, bioavailability to animals and humans, interrelationship of Cd to other elements related to growth and nutrition, accumulation in organs in relation to age of humans, and diet.

Considerable research has been conducted on Cd in biosolids and potential health impacts. This section highlights some of the key aspects. For greater details, the author encourages readers to explore works by Ryan et al. (1982); Friberg et al. (1974) and Elinder (1985).

Animals and Humans

Cadmium is not considered essential to animals and man. However, limited data suggest the contrary — that this element may be essential (NRC, 1980). Cadmium

is toxic to animals and man. It is retained in the kidney and liver and is probably related to the metal binding protein metallothionein (Kagi and Vallee, 1960).

Acute health effects due to high exposure can result in severe damage to several organs. The data are primarily from experiments with animals and occupational exposure. Cd exposure in fumes (e.g., in plating operations) can result in pulmonary edema. Lucas et al. (1980) reported on lethal effects of Cd fumes. Acute symptoms by Cd fumes occur after 4 to 6 hours of exposure and include cough, shortness of breath and tightness of chest. Pulmonary edema may appear within 24 hours, often followed with bronchopneumonia (Ryan et al., 1982).

The accumulation of Cd in the body appears to increase up to the age of 50 and then decreases (Elinder et al., 1976). It has been estimated that the half-life of Cd in the kidney ranges from 18 to 33 years (NRC, 1980). Chronic health effects are principally manifested in the kidney. Other chronic health effects believed to be related are; hypertension, respiratory effects, carbohydrate metabolism, carcinogenesis, teratogenesis and damage to liver and testicles.

Scientists disagree about the effects of cadmium on cancer. After reviewing the literature, Fasset (1975) states that the evidence for carcinogenesis appears to be doubtful. Sunderman (1971, 1978) also found the evidence on cancer to be meager. Kolonel (1976) compared 64 cases of renal cancer in white males with controls and indicated significant association of renal cancer to exposure to cadmium. Several authors indicate a relationship between the formation of Leydig-cell tumors in testes of animals (Reddy et al., 1973; Levy et al., 1973; Malcolm, 1972).

Adsorbed Cd is bound to a low-molecular-weight protein to form metallothionein, which accumulates in the kidney cortex (Chaney, 1983). Also, Cd apparently competes with Zn on the same binding sites, presumably thiol groups (Pulido et al., 1966). Renal chronic effects are manifested by proteinuria and tubular dysfunction. Friberg et al. (1974) estimated that the critical level of damage in the renal cortex is 200 µg/g wet weight.

Other than occupational exposure, the intake of Cd is principally from food and water and, in the case of smokers, from smoking. Gastrointestinal adsorption is poor. It is estimated that approximately 5% of the intake of Cd is adsorbed through the gut (WHO, 1982; Shaikh and Smith, 1980).

The tobacco plant accumulates Cd in the leaves as a result of its presence in the soil and concentrations can range from 1 to 6 µg/g. The primary source is from phosphate fertilizers. Furthermore, tobacco is grown on acidic soils, which enhance the availability and plant uptake of Cd. Each cigarette can contain from 1.2 to 2.0 µg/g Cd. Cigarette smoke can be a very significant source of Cd to the body because adsorption through the lung is high. Friberg et al. (1974) estimated that nearly 50% of the Cd in cigarette smoke is absorbed. Higher values have been suggested. Thus for smokers, more than one-third of the body burden could be from smoking. An individual who smokes one pack of cigarettes per day could receive about one-half of the body burden of Cd from this source. Sharma et al. (1983) demonstrated that cigarette smoking had a more pronounced and significant effect on whole blood Cd levels than intake from ingestion of oysters that have high Cd concentrations. [Table 4.7](#) shows the potential intake of Cd from various sources.

Table 4.7 U.S. Daily Intake and Retention of Cadmium from Various Sources

Source	Concentration	Intake μg	Retained $^1\mu\text{g}$
Total diet	0.04 $\mu\text{g/g}$	51	2.30
Drinking water	0.0014 $\mu\text{g/g}$	2.8	0.13
Air	0.006 $\mu\text{g/m}$	0.12	0.05
Cigarettes (20)	1.0 $\mu\text{g/g}$	3.1	1.4

¹ Assuming 4.5% of ingested Cd and 45% of inhaled Cd are retained.

Source: Parr et al., 1977.

The risk reference dose (RfD) for Cd is 70 $\mu\text{g/day}$. This RfD is designed to protect the highly exposed individuals (Chaney and Ryan, 1993). This level is also the maximum permissible level of dietary Cd established by the World Health Organization.

Daily intake of Cd varies. It has been estimated that the variation ranges from 12 $\mu\text{g/day}$ to 51 $\mu\text{g/day}$ (Braude et al., 1975; Ryan et al., 1982; Chaney and Ryan, 1993).

Although there is no evidence that human exposure to Cd from biosolids applied to land has resulted in health effects, there is strong evidence of adverse health effects from exposure to contaminated foods. A prominent example relating Cd contamination of food crops and water occurred in Japan. In 1955 Drs. Hagino and Kohno (Yamagata and Shigematsu, 1970) reported on a disease they named "Itai-itai" or "ouch-ouch," which was the result of severe bone pains. The disease was manifested by osteomalacia, pathologic features similar to Fanconi's Syndrome and pain in inguinal (groin) and lumbar regions and joints. Other manifestations were proteinuria and glycosuria and an increase of serum alkaline-phosphate and decrease of inorganic phosphorus. Duck gait was evidenced as well as roentgenological appearance of the transformation zone of the bone with proneness to fracture. The affected individuals were primarily childbearing women over 40 years of age.

In 1968, the Japanese Ministry of Health and Welfare reported that the disease was caused by chronic Cd poisoning. Cadmium polluted rice fields were the result of discharges from mine smelting activities. Inhabitants accumulated Cd from food and water. Yamagata and Shigematsu (1970) found paddy-soil levels of Cd between 2.2 and 7.2 parts per million (ppm) and rice levels between 0.72 and 4.17 ppm as compared with control levels of less than 1 ppm in soil and 0.03 to 0.11 ppm in rice. The latter are relatively low levels in both soils and crops in terms of potential toxic effects on humans. More recent data have shown that the Japanese conditions have been greatly affected by their diet and the bioavailability of Cd. The Japanese consume large quantities of rice. A typical consumption of 300 g per day of rice containing 1 ppm of Cd would result in an addition of 300 mg Cd.

McKenzie and Eyon (1987) and McKenzie et al. (1988) reported that New Zealand adults in a region of that country consumed large quantities of dredge or bluff oyster (*Tiostrea lutaria*) which has a high concentration of Cd. Consumption of Cd from oysters and fecal output of Cd in some New Zealand adults exceeded

the fecal output reported by the Japanese. However, the New Zealand residents did not have renal damage or symptoms similar to the Japanese residents. The main differences between the two populations were their diets and the bioavailability of Cd in different foods or diets (Chaney and Ryan, 1993). Other studies in England (Sherlock, 1984) and East Greenland (Hansen et al., 1985), where populations consumed high levels of Cd, did not show adverse health effects.

Fox (1988) indicates that Zn, Fe, Cu, Ca, ascorbic acid and protein may interact with dietary Cd. Iron particularly affects the bioavailability of Cd. Low Fe diets contributed to higher Cd retention (Flanagan et al., 1978). Increased dietary Zn apparently induces biosynthesis of metallothionein, which binds both Cd and Zn (Chaney, 1988). Calcium deficiency also increases Cd adsorption (Chaney, 1988). Thus, the potential effect of Cd from food crops is not only a function of levels in the crops but also Cd bioavailability and human nutrition conditions.

Soil

In soil of nonpolluted areas, Cd is usually less than 1 mg/kg dry weight (Page et al., 1981). However, high levels of Cd have been found in certain areas as a result of geological parent material sources (Lund et al., 1981). As indicated earlier, the extensive evaluation of agricultural soils in the United States by Holmgren et al. (1993) found levels of Cd ranged from <0.0010 to 2.0 mg/kg (Table 4.2). Andersson (1976) reported that, in 361 Swedish soil samples, Cd ranged from <0.063 to 0.249 µg/g. Cd concentrations in soil are dependent on the parent material, secondary material and organic substances (Elinder, 1985). Cd mobility and uptake by plants is affected by soil pH, organic matter, iron and clay.

Plants

Cadmium is not essential to plants and its toxicity is generally moderated (Gough et al., 1979). Depressed growth of plants appears to be when plant tissue Cd exceeds 3 µg/g (Allaway, 1968; Millner et al., 1976). Bingham (1979) indicated that a 25% yield reduction for various crops resulted when Cd concentration ranged from 7 to 160 µg/g dry weight. Uptake, accumulation and translocation of Cd by plants varies considerably (CAST, 1980; Bingham, 1979; Bingham et al., 1975, 1976; Chaney and Hornick, 1978; Chaney, 1983; Dowdy and Larson, 1975). Accumulation varies between plants and within plants. Different organs of the plants studied accumulated Cd to varying degrees. Primarily, Cd accumulates in leaves (Chaney and Hornick, 1978; Bingham et al., 1975, 1976). Detailed information is presented in Chapter 5. Tobacco, as a leafy plant grown on acidic soils, accumulates Cd. Chaney et al. (1978) reported that tobacco grown on biosolid-amended soil accumulated 44 µg/g when the soil contained 1 µg/g of Cd. Smoking is a major source of Cd in the body.

Cadmium uptake by plants is affected by several soil factors including pH, organic matter, soil particle size, chloride concentration, total soil Cd, Zn status, hydrous iron and the presence of manganese and aluminum oxides (Brown et al., 1996; McBride, 1995; McLaughlin et al., 1994; Corey et al., 1987).

Chromium (Cr)

Animals and Humans

Chromium is essential to animals and man (Underwood, 1977; NRC, 1980). For example, it is necessary for normal glucose metabolism in animals (Van Campen, 1991). Humans are often deficient in this element as a result of low levels in plants. An organic form of the element is a cofactor in insulin response controlling carbohydrate metabolism (Toepfer et al., 1977). Chromium does not appear to concentrate in any specific organ. However, it was found to accumulate in the lung, probably as a result of inhalation of dust containing Cr (Mertz, 1967).

Chromium tends to decline in body tissues with age (Anderson and Koslovsky, 1985). Anderson (1987) indicates that Cr deficiency affects glucose intolerance, elevated serum cholesterol and elevated serum triglycerides. Other manifestations include elevated blood-insulin concentrations, glycosuria, hyperglycemia, neuropathy and encephalopathy. Several foods that are good sources of Cr include brewer's yeast, meat, cheese and whole grains. Chromium as chromium picolinate is sold as a dietary supplement.

Chromium is also toxic. Certain chemical forms have been shown to be mutagenic and carcinogenic. Chromate in dusts and mist has been shown to result in nasal cancer (NRC, 1980). Occupational manifestations of cutaneous and nasal mucous-membrane ulcers and contact dermatitis have been reported following exposure to hexavalent chromium (Gough et al., 1979). Van Campen (1991) indicates that trivalent Cr at the dietary levels normally encountered is not likely to be toxic.

Soils

Chromium exists in soils in low redox forms: chromic (Cr^{3+}) and chromate (Cr^{6+}). Chromate is rapidly reduced to chromic in soils. This reduction occurs more rapidly in acidic soils (Bartlett and Kimble, 1976; Cary et al., 1977). Chromium is strongly adsorbed and chelated by soils. Chromic is insoluble and also strongly sorbed. These reactions reduces its presence in the soil solution and reduces plant uptake. Chromate is rapidly reduced to Cr^{3+} by reaction with organic matter or other reducing agents in soils. However, Bartlett and James (1979) showed that Cr^{3+} can be oxidized to Cr^{6+} by Mn-oxides.

The inert nature of Cr compounds and chelates (slow kinetics of reactions in soils) can be important in limiting the potential for oxidation of applied Cr^{3+} and leaching of Cr^{6+} . Equilibrated Cr^{3+} in soils is essentially inert under the conditions of pH, chelation and redox found in nearly all soil materials. If Cr^{3+} is only sparingly soluble in the soil solution, the oxidation reaction does not proceed. This inert nature is an important source of environmental protection against adverse effects of Cr^{3+} applied to soil by biosolids or other organic amendments (Chaney et al., 1996).

Plants

Chromium is nonessential to plants. It is phytotoxic as chromate (Cr^{6+}). Chromium toxicity varies greatly with species. On some soils high in Cr (e.g., serpentine soils), several species tolerate the high levels of Cr. Chromate is more soluble and more available for plant uptake than Cr^{3+} usually found in biosolids. Chromium has produced toxicity symptoms to tobacco, corn and oat at soil chromate levels of 5 to 16 ppm (NRC, 1974). In tobacco, symptoms occurred when concentrations in leaves ranged from 18 to 24 mg/kg and 375 to 410 mg/kg in roots. Corn leaves exhibited symptoms at 4 to 8 mg/kg; and oats at 252 mg/kg (NRC, 1974).

Cr^{6+} phytotoxicity is manifested by reduced root development. Cumulative application of Cr in biosolids had occurred in the field in the United States at least as high as 300 kg/ha without adverse effects (Chaney et al., 1996). Long-term studies in Minnesota indicated that there was no reduction in corn yield nor in Cr accumulation when 1045 tonnes/ha of Cr were applied through biosolids (Dowdy et al., 1994).

Plant uptake of Cr is very limited because it is reduced in the roots to Cr^{3+} and is not translocated to the above portions of the plant. Even under Cr^{6+} phytotoxicity, the level of Cr is less than 10 mg/kg. Because crops have low Cr levels even if grown on soils very high in Cr, the food chain is protected against excess Cr in plant tissues. Plants grown on serpentine soils containing as much as 1% (10,000 mg Cr/kg) do not exhibit Cr phytotoxicity (Chaney et al., 1996).

Copper (Cu)

Copper has been used for decades as an algicide and fungicide. Bordeaux (a mixture of copper sulfate and lime) has been used as a spray in vineyards and vegetable crops. Copper has also been added as diet additive to swine and poultry and thus excreted in the manure. Industrial pollution also added Cu to soils. Cu deficiencies in agriculture are more common than toxicities. Cu is often added to agricultural crops grown on sandy soils.

Animals and Humans

Copper is essential to animals and man. Cu is associated with Cu proteins and enzymes. Cu appears to be essential for normal reproduction (Underwood, 1981). Copper is also toxic to animals. Toxicity to sheep and cattle has been reported to occur at levels of 25 to 100 mg/kg dry diet (NRC, 1980). Sheep appear to be particularly sensitive to copper. Relatively high concentrations are found in the liver, brain, heart and hair (Miller et al., 1991).

Cu is toxic to man but poisoning is rare. It is concentrated in the liver and depends on age and diet (Van Campen, 1991). Wilson's disease is caused by the buildup of Cu in the liver and central nervous system as a result of the body's inability to excrete it (Scheinberg, 1969). Acute poisoning causes gastrointestinal ulcerations, hepatic necrosis, hemolysis and renal damage (Van Campen, 1991).

Cu deficiencies include anemia associated with Fe adsorption and utilization; bone and cardiovascular disorders, mental and/or nervous system deterioration and defective keratinization of hair (Van Campen, 1991). Oysters, organ meats, mushrooms, nuts and dried legumes are considered a good source of dietary Cu (Van Campen, 1991).

Marston (1950) noted that Cu deficiency in animals inhibited hemoglobin formation. It was found that Cu was not actually part of the hemoglobin molecule, but it performs an important function in the formation of hemoglobin.

Soils

Cu is a very immobile micronutrient in the soil (Moraghan and Mascagni, 1991). Its reaction in soil is similar to several other metals. A low soil pH increases Cu solubility and availability to plants. Soil organic matter binds Cu to form complex chelates (Logan and Chaney, 1983). Optimum acidity for the complex formation of Cu ranges from pH 2.5 to 3.5 for humic acid and pH 6 for fulvic acid. The reaction of Cu (II) with carboxyl groups in humic acid has been suggested by Schnitzer (1978) and Boyd et al. (1981). Chaney and Giordano (1977) cited several cases of reversion of Cu to unavailable forms. Organic soils such as peats and mucks generally have low available Cu or the Cu is complexed resulting in crop deficiencies.

Plants

Copper in the water-soluble and exchangeable forms is considered available to plants (Shuman, 1991). The normal range of Cu in plants is from 5 to 20 mg/kg in tissues. Phytotoxicity occurs in most plants at about 25 to 40 mg/kg dry foliage (Chaney and Giordano, 1977; Page, 1974).

Cu toxicity is manifested by dark green leaves followed by induced Fe chlorosis, thick, short, or barbed-wire looking roots and depressed tillering (Jones, 1991). Toxic levels of Cu in plants are dependent on the concentration of clay and organic matter.

Cu is contained in enzymes and plant proteins. It plays an important part in photosynthesis and respiration. In many species Cu concentrations of less than 5 mg/kg are indicative of deficiency. Cu deficiency results in depressed growth and reproduction (i.e., formation of seeds and fruits). Deficiency symptoms are chlorosis (white tip, reclamation disease), necrosis, leaf distortion and dieback. The most noticed symptoms of Cu deficiency are reduced seed and fruit production as a result of male sterility (Romheld and Marschner, 1991). Phosphate, manganese, or zinc may directly compete with available Cu, potentially resulting in Cu deficiency. Other factors that could affect Cu concentration in plants are microbial activity, moisture, pH, redox potential and plant species.

Lead (Pb)

Animals and Humans

Lead is a nonessential element to humans, animals and plants. It is toxic to humans and in the past several decades there has been an increased concern for its toxicity to children. There are many sources of Pb exposure to humans. Air, water, dust, soil and diet are the primary sources.

The acceptable blood levels have become more restrictive over the years. In 1985 the acceptable blood level was 25 µg/dl, whereas in 1991, it was reduced to 10 µg/dl (CDC, 1991). Its toxicity is based on body weight. Generally, toxic intake is 1 mg, lethal intake is 10 g (Pais and Jones, 1997). Lead toxicity to many animals occurs at about 30 mg Pb/kg diet (NRC, 1980). Dietary Fe, Ca, Zn, P and fiber interact with Pb (Mahaffey and Vanderveen, 1979; Levender, 1979).

The primary risk to animals and man is from ingestion of particles with high concentration of Pb. U.S. Environmental Protection Agency, in conducting risk assessment on land application of biosolids, determined that soil ingested by children represents the highest level of risk. Soil Pb can result in excessive blood Pb if it is somewhat bioavailable to humans (Chaney, 1983). Adsorption of dietary Pb, especially the inorganic forms, is decreased by increasing dietary levels of Ca, P, Fe and Zn. In ruminants, tolerance of dietary Pb is increased by added levels of dietary sulfur or sulfate. Se sometimes also provides protection.

Soils

Soils throughout the world contain Pb. Some of the Pb in soils is from natural geological sources whereas other soils have become polluted or contaminated by man. Soils throughout the world have been polluted and contaminated with Pb from leaded gasoline, paints and emission sources. The past use of organic Pb additives to gasoline is the major source of Pb contamination of surface soils.

Geochemical concentrations of lead (Pb) in the earth's crust have been estimated at 12.5 mg/kg (*CRC Handbook of Chemistry and Physics*, 1990). Pb concentration in natural soils was reported by Conner and Shacklett (1975) to range from 2.6 to 25 mg/kg and Holmgren et al. (1993) reported that Pb in agricultural soils range from <1 to 135 mg/kg with a mean of 10.5 mg/kg. Pais and Jones (1997) indicated that the total content of Pb in soils ranged from 3 to 189 mg/kg, and the natural background level ranged from 10 to 67 mg/kg.

Pb does not readily move through the soil profile. Numerous studies have shown that it remains on or near the soil surface (Chaney et al., 1988). This feature has both positive and negative attributes. By remaining at the surface and not moving through the soil profile the potential for contamination of ground water resources and drinking water is very low. However by remaining at the surface, the potential exposure to children by ingestion of soils or by dust is much greater. Lead in surface soils stems primarily from the use of Pb additives to gasoline and atmospheric deposition from industrial sources. Surfaces painted with lead-based paint also can be an important source of soil Pb.

The reaction of Pb in soil is affected by adsorption by the soil cation exchange complex; precipitation by sparingly soluble compounds; and formation of relatively stable complex ions or chelates as a result of interaction with the soil organic matter. The degree of sorption will depend on the soil's electronegativity and the ionization potential of the adsorbed ions as well as the exchange complex. Lead solubility in soil decreases as the soil pH increases. In noncalcareous soils, the solubility of Pb appears to be related to the formation of hydroxides and phosphates [e.g., $\text{Pb}(\text{OH})_2$, $\text{Pb}_3(\text{PO}_4)_2$]. In calcareous soils, lead carbonate (PbCO_3) appears to be dominant.

Lead combines with ligands to form stable metal complexes and chelates and in this matter is complexed with soil organic matter. In a letter to the USDA, Chaney suggested that the use of biosolids products in urban areas where Pb concentration from automobile emissions is high could reduce its availability to children ingesting soil.

Plants

Lead is not essential to plants. Phytotoxicity to plants is rare although elevated levels in plants have been reported. Plants growing in soils in lead-rich sites absorbed large amounts of Pb without exhibiting phytotoxicity (Shacklette, 1960). On lead-mined soils, high levels have been found in grasses (Johnson and Proctor, 1977). Baumhardt and Welch (1972) applied up to 3200 kg/ha of Pb to a soil with a pH of 5.9 and did not observe a decrease in corn yield.

Plants can take up Pb into the roots; however little is generally translocated to the upper portion of the plants because insoluble Pb-phosphate is formed in the roots. As a result, the food chain is protected from excess lead.

Mercury (Hg)

Mercury is nonessential to plants, animals and humans. It has been widely used as a fungicide in agriculture and horticulture. Hg compounds inhibit bacterial growth and have been used as antiseptics and disinfectants (Gough et al., 1979).

Animals and Humans

Mercury is toxic and is not essential to animals and man. Methylated mercury is the most toxic form. Methyl mercury (MeHgOH) is a neurotoxin (WHO, 1990). Mercury poisoning of humans from fish and contaminated seed have been reported (Friberg and Vostal, 1972; Bakir et al., 1973)

Soils

Mercury reaches the soil from atmospheric deposition, use of fungicides or insecticides and wastes. Once in the soil, Hg reacts with the exchange complex of the clay and organic fractions, forming both ionic and covalent bonds. It can be precipitated as insoluble phosphate, carbonates and sulfides. Mercury can be chelated to organic matter. The binding of Hg to organic matter and clay reduces its potential

for groundwater contamination. Many mercurial compounds, both organic and inorganic, can be volatilized, converted to sulfur and chloride compounds, or adsorbed by sesquioxide surfaces. Oxidized Hg can be reduced to volatile Hg⁰ in the upper surface layer of soil (Carpi and Lindberg, 1997). Sunlight, surface soil temperature and soil moisture are factors that affect Hg emissions (Carpi et al., 1997). Liming a soil to a pH exceeding 6.5 reduces its availability to plants.

Plants

Mercury can enter plants through the roots and leaves from foliar sprays, dusts, or vapors. Mercury in plant tissues is principally organic and primarily as methyl mercury. It is soluble in water and is available for incorporation into tissues of aquatic organisms (Gough et al., 1979). Toxicity to greenhouse plants from volatilized elemental Hg has been observed (Shacklett, 1970).

Molybdenum (Mo)

Animals and Humans

Molybdenum is essential to animals and man. It functions as molybdoflavo-protein in maintenance of levels of xanthine oxides. Deficiencies have been reported in sheep (Underwood, 1977; NRC, 1980). Molybdenum is toxic to animals — especially ruminants. Monogastric animals are more tolerant of Mo than ruminants. In sheep, the highest concentration of Mo accumulates in the liver, followed by the kidney and then the lung (Grace and Martinson, 1985).

Molybdenosis occurs as a result of induced Cu deficiency as well as excess Mo and low sulfate-Se concentrations in forage (Mills and Davis, 1987; Underwood, 1977; Gough et al., 1979). This disease is also referred to as teart disease or peat scours. Mo supplements can alleviate chronic Cu toxicity in sheep (NRC, 1980). Mo in animals is also important in enzyme metabolism (Miller et al., 1991). Both increased growth (Payne, 1977) and decreased growth (Anke et al., 1985) have been reported. Yang et al., (1985) indicated that Mo in drinking water inhibited mammary carcinogenesis.

Molybdenum toxicity in humans is rare. Gough et al. (1979) cite a case in India where individuals consumed sorghum that was grown on alkali soils high in Mo. The peasants developed a crippling syndrome of knock-knees (*genu valgum*).

Soils

Molybdenum is associated with both the organic and inorganic soil fractions and is often found with iron oxides. It is sorbed by sesquioxides (especially iron) and clay minerals. The amount of Mo absorbed by clays and hydrous oxides decreases with increasing soil pH to about 7.5, after which limited absorption takes place. Increasing the soil pH by liming from pH 5 to pH 7 increased Mo uptake by plants.

Molybdenum is present in soils as anionic molybdate. Soils adsorb Mo strongly under acidic conditions (Chaney, 1983). Therefore under acidic conditions Mo does

not readily leach through the soil. In acid soils Fe-molybdates are the predominant form of inorganically combined Mo. Iron oxides and P in soils greatly affect Mo sorption. Large quantities of P in the soil will replace Mo, which is bound to iron oxides. Maximum sorption of Mo occurs in soils at pH 4.2 (Cast, 1976).

In well-aerated soils, the predominant chemical forms are MoO_4^{2-} and HMO_4^{1-} . Under alkaline conditions, Mo is more readily taken up by plants and also can leach through the soil. Several soils are high in Mo resulting in molybdenosis of sheep and cattle (Kabota, 1977; Gupta et al., 1978). Molybdenosis has been found in Kern County, California, the San Joaquin Valley of California, Nevada and Oregon (Barshad, 1948; Kabota et al., 1961, 1967).

Plants

Molybdenum is an essential trace element for plants. It is contained in several enzymes, including sulfite oxidase, aldehyde oxidase, and xanthine dehydrogenase. It is also present in the enzyme nitrogenase, which is responsible for molecular nitrogen formation and in the nitrate reductase enzyme, which is responsible for nitrification. Plants suffering from Mo deficiency often exhibit signs of N deficiency.

Plants can tolerate high levels of Mo and translocate it to the edible portions. Molybdenum content of plants varies. Legumes accumulate more Mo than grasses (Allaway, 1977; Kabota, 1977). Forage plants have been shown to contain 200 mg/kg Mo, which is more than 600 times the amount necessary for growth (Evans et al., 1950). Vegetables can also accumulate Mo (Gupta et al., 1978). The Mo availability to plants is closely related to the kinds and amounts of Fe compounds in the soil.

Gerloff et al. (1959) and Olsen and Watanbe (1979) indicated that in alkaline and calcareous soils of semiarid regions, high Mo concentrations may result in plant induced Fe deficiency indicated by chlorosis. Molybdenum accentuated Fe deficiency at low levels of available Fe. Hence this interaction of Fe and Mo may be significant in alkaline soils where pH impacts Fe availability and native soils are high in Mo.

Molybdenum deficiency symptoms manifest in malformation of leaves (whiptail), interveinal mottling and marginal chlorosis of older leaves, followed by necrotic spots at leaf tips and margins (Romheld and Marschner, 1991). Mo deficiency results in destruction of embryonic tissues. Deficiency generally occurs in various plant tissues when concentrations are in the range of 0.03 to 0.15 mg/kg.

Molybdenum toxicity manifests itself through yellowing or browning of leaves and depressed tillering. Toxicity generally occurs when plant tissue of mature leaves is >100 mg/kg (Jones, 1991). Molybdenum availability to plants is primarily influenced by the level of Mo, sulfate, phosphate, pH, and the nature and content of free Fe-oxides.

Nickel (Ni)

Nickel is essential to plants, animals and man. The greatest concern in biosolids relates to potential phytotoxicity. Ni is ubiquitous in the environment. Application

of phosphorus fertilizers, coal, fly ash and biosolids can increase soil Ni and result in an increase in plant uptake.

Animals and Humans

Ni is an essential micronutrient for animals (Nielsen, 1984). However, deficiency has seldom been observed. Ni is toxic to animals and occurs at 50 to 100 mg Ni/kg feed where Ni is added as soluble salts (NRC, 1980). Its toxicity to mammals is low, possibly as a result of limited absorption (Gough et al., 1979). Animals appear to have a higher tolerance to Ni than do plants. Therefore there appears to be little possibility of Ni toxicity to animals consuming Ni at levels that are phytotoxic to plants.

The levels in biosolids do not appear to endanger animals consuming crops grown on biosolids-applied land. Phytotoxicity would reduce plant growth prior to reaching Ni levels that could be harmful to animals and man. Toxicity to humans is low. Occupational pathogenic evidence has been observed.

Soil

Nickel is found in all soils. There is a great variation in Ni content of soils, ranging from 5 to 500 mg/kg (Swaine, 1955). Soils that contain the mineral serpentine may have levels up to 500 mg/kg (Asher, 1991). Soil can be contaminated with nickel from superphosphate, automobile exhausts, industrial smokestacks, smelting and biosolids. The soil chemistry of nickel is similar to that of many metals. Factors such as cation exchange capacity (CEC), organic matter, chelation, pH, solubility and precipitation are important in determining the availability of Ni to plants. The concentration of extractable Ni in soil appears to be governed by the Fe and Mn hydrous oxide surfaces that act as a sink for Ni and by organic chelates that complex Ni (Cast, 1976).

Plants

Ni was shown to be a trace constituent of plants and beneficial since the mid 1920s (Asher, 1991). Its essentiality was demonstrated in 1987 when (Brown et al., 1987a; 1987b) described deficiency symptoms in wheat, oats and barley. These included interveinal chlorosis, premature senescence and inability of the leaves to completely unfold. Ni appears to be important in urea metabolism and involved in enzymatic reactions.

Ni toxicity manifests itself in chlorosis and yield reduction. Cunningham et al. (1975) found that increasing Ni content in biosolids significantly increased tissue Ni content. However no toxicity was observed when 81 mg/kg in biosolids and 100 mg/kg Ni as NiSO_4 were applied to soil. Phytotoxicity manifests in interveinal chlorosis of young leaves at about 50 to 100 mg/kg dry weight (Chaney, 1983). Some plants are tolerant of Ni and are Ni accumulators, where concentration can exceed 1000 mg/kg (Asher, 1991).

Selenium (Se)

Se is both beneficial and toxic to plants, animals and humans (McNeal and Balistrieri, 1989). Se is found in virtually all geological materials on earth and is a component of soils due to weathering of rocks. It enters the atmosphere and the environment from volcanic activity and burning of fossil fuel, especially coal (McNeal and Balistrieri, 1989). Several areas in the United States contain high Se concentrations in soils, resulting in Se toxicity to cattle. These areas are mostly in western states and are associated with known seleniferous geological formations (Boon, 1989).

The application of biosolids to agricultural soils did not increase Se uptake by plants (Dowdy et al., 1994; Logan et al., 1987).

Soil

The concentration of Se in most soils ranges from 0.01 to 2 mg/kg. There are, however, areas in the world where reported values exceed 1200 mg/kg (Swaine, 1955). Soil pH and redox potential affect the forms of Se (Chaney, 1983; Elrashidi, et al., 1989). Selenate is the major species in the soil solution and therefore is readily absorbed by plants. Selinite is adsorbed on soil and is only marginally available to plants.

Plants

Se is not considered essential for all plants (Gough et al., 1979). Plants grown on seleniferous soils can absorb large amounts of Se. Mayland et al. (1989) reported that certain species can have concentrations of Se in the hundreds or thousands of mg/kg. Resistance to Se toxicity varies considerably so that general toxicity levels cannot be reliably estimated (Gough et al., 1970).

Zinc (Zn)

Animals and Humans

Zn is essential to animals and humans and is an indispensable component of more than 200 enzymes and proteins (Hambridge et al., 1987). There have been several examples of Zn deficiency reported (Prasad et al., 1963; Hambridge et al., 1972).

Zinc is a requirement for all species of animals that have been examined. Requirements for young domestic animals and poultry range from 40 to 100 mg/kg in natural diets (NRC, 1980). Higher levels are required when diets contain excessive calcium and especially when also combined with vegetable proteins and excessive phytate. Zinc requirements and tolerance to Zn are affected by several nutrients including vitamin A and D, Cu, Mn, Fe, Pb and Cd.

Soil

The primary natural source of Zn in soils is from weathering of the ferromagnesian minerals and sphalerite (Chesworth, 1991). Zn is also introduced to agricultural soils from phosphate fertilizers as well as atmospheric deposition. Soil clays, organic matter and hydrous oxides play a major role in the retention and adsorption of Zn (Harter, 1991).

Plants

Zinc is essential and can also be toxic to plants. Staker and Cummings (1941) reported toxicity on spinach, lettuce and carrots grown on peat soils in New York. The concentration of Zn in plant species varies widely. Zn deficiency in plants as a result of low Zn in soil occurs in many of the cropping areas of the United States and throughout the world (Bould et al., 1984; Welch et al., 1991). Chapman (1966) indicated that Zn deficiencies in plants occurred when Zn levels were less than 20 to 25 mg/kg dry matter. Usually Zn deficiency in plants is associated with high-pH soils or with coarse-textured, highly leached acid soils (Welch et al., 1991).

CONCLUSION

Many of the regulated heavy metals are essential to animal and human health and plant growth. An element such as zinc is often deficient in soils and, as a result, affects crop production. This same element is vital to human development. The use of biosolids can often alleviate plant micronutrient deficiencies.

Other heavy metals or trace elements are toxic to animals, humans and plants. Their addition to soils through land application should be minimized. As indicated in [Chapter 1](#), due to industrial pretreatment during the past decade, heavy metals have been significantly reduced in biosolids.

REFERENCES

- Allaway, W.H., 1968, Agronomic controls over the environmental cycling of trace elements, pp. 235–274. A.G. Norman (Ed.), *Advances in Agronomy*, vol. 20, Academic Press, New York.
- Allaway, W.H., 1977, Perspectives on molybdenum in soils and plants, pp. 317–339, W.R. Chappell and K.K. Petersen (Ed.), *Molybdenum in the Environment*, Marcel Dekker, New York.
- Anderson, R.A., 1987, Chromium, pp. 225–224. W. Mertz (Ed.), *Trace Elements in Human and Animal Nutrition*, 5th ed., vol. 1, Academic Press, San Diego, CA.
- Anderson, R.A. and A. Koslovsky, 1985, Chromium intake, absorption and excretion of subjects consuming self-selected diets, *Am. J. Clin. Nutr.* 41: 1177–1183.
- Andersson, A. and K.O. Nilsson, 1976, Influence on the levels of heavy metals in soil and plant from sewage sludge used as a fertilizer, *Swedish J. Res.* 6: 151–159.

- Anke, M., B. Groppel and M. Grun, 1985, Essentiality, toxicity, requirements and supply of molybdenum in humans and animals, pp. 154–157. C.F. Mills et al., (Ed.), *Trace Elements in Man and Animals* – TEMA5, Commonwealth Agric. Bureaux, Farnham, England.
- Asher, C.J., 1991, Beneficial elements and functional nutrients, pp. 703–723, J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI.
- Ashworth, W., 1991, *The Encyclopedia of Environmental Studies*, Facts on File, New York.
- Bakir, K., S.F. Damluji, L. Amin–Zaki, M. Murtadha, A. Khalidi, N.Y. Al–Rawi, S. Tikriti, H.I. Dhahir, T.W. Clarkson, J.C. Smith and R.A. Doherty, 1973, Methylmercury poisoning in Iraq, *Science* 181: 230–241.
- Barshad, I., 1948, Molybdenum content of pasture plants in relation to toxicity to cattle, *Soil Sci.* 6: 187–195.
- Bartlett, R.J. and J.M. Kimble, 1976, Behavior of chromium in soils: II, Hexavalent forms, *J. Environ. Qual.* 5: 383–386.
- Bartlett, R.L. and B. James, 1979, Behavior of chromium in soils: III, Oxidation, *J. Environ. Qual.* 8: 31–35.
- Baumhardt, G.R. and Welch, L.F., 1972, Lead uptake and corn growth with soil applied lead, *J. Environ. Qual.* 1: 92–94.
- Berthelsen, B.O., E. Steinnes, W. Solberg and L. Jingsen, 1995, Heavy metal concentrations in plants in relation to atmospheric heavy metal deposition, *J. Environ. Qual.* 24: 1018–1026.
- Bingham, F.T., 1979, Bioavailability of Cd to food crops in relation to heavy metal content of sludge–amended soil, *Environ. Health Perspect.* 28: 39–43.
- Bingham, F.T., A.L. Page, R.J. Mahler and T.J. Ganje, 1975, Growth and cadmium accumulation of plants grown on a soil treated with cadmium–enriched sewage sludge, *J. Environ. Qual.* 4: 207–211.
- Bingham, F.T., A.L. Page, R.J. Mahler, and T.J. Ganje, 1976, Yield and cadmium accumulation of forage species in relation to cadmium content of sludge–amended species, *J. Environ. Qual.* 5: 57–60.
- Bingham, F.T., A.L. Page, R.J. Mahler, and T.J. Ganje, 1976, Cadmium availability to rice in sludge–amended soil under “flood” and “nonflood” culture, *Soil Sci. Soc. Am. J.* 40: 715–719.
- Boon, D.Y., 1989, Potential selenium problems in Great Plains soils, pp. 107–121, L.W. Jacobs (Ed.), *Selenium in Agriculture and the Environment*, American Society of Agronomy, Madison, WI.
- Bould, C., E.J. Hewitt and P. Needham, 1984, *Diagnosis of Mineral Disorders in Plants*, Chemical Publ., New York.
- Bowhay, D. 1997, Screening survey for metals in fertilizers and industrial by–product fertilizers in Washington State, Dept. of Ecology, Ecology Publ. 97–341, Olympia, Washington.
- Boyd, S.A., L.E. Sommers and D.W. Nelson, 1981, Copper (II) and iron (III) complexation by the carboxylate group of humic acid, *Soil Sci. Soc. Am. J.* 45: 1241–1242.
- Braude, G.L., C. Jelinek, and P. Corneliussen, 1975, FDA’s overview of the potential health hazards associated with land application of municipal wastewater sludge, *Proc. Second National Conf. on Municipal Sludge Management and Disposal*, Information Transfer, Inc., Rockville, MD, 214–217.
- Brown, P.H., R.M. Welch and E.E. Cary, 1987a, Nickel: a micronutrient essential for higher plants, *Plant Physiol.* 85: 801–803.

- Brown, P.H., Welch, R.M., Cary, E.E. and Checkai, R.T., 1987b, Beneficial effects of nickel on plant growth, *J. Plant Nutr.* 10: 2125–2135.
- Brown, S.L., R.L. Chaney, C.A. Lloyd, J.S. Angle, and J.A. Ryan, 1996, Relative uptake of cadmium by garden vegetables and fruits grown on long-term biosolid-amended soils, *Environ. Sci. Technol.* 30: 3508–3511.
- Carpi, A. and S.E. Lindberg, 1997, The sunlight mediated emission of elemental mercury from soil amended with municipal sewage sludge, *Environ. Sci. Technol.* 31: 2085–2091.
- Carpi, A., S.E. Lindberg, E.M. Prestbo and N.S. Bloom, 1997, Methyl mercury contamination and emission to the atmosphere from soil amended with municipal sewage sludge, *J. Environ. Qual.* 26: 1650–1655.
- Cary, E.E., W.H. Allaway and O.E. Olson, 1977, Control of chromium concentration in food plants, II: Chemistry of chromium in soils and its availability to plants, *J. Agr. Food Chem.* 25: 305–309.
- Case, A.A., 1974, Toxicity of various chemical agents to sheep, *J. Am. Vet. Med. Assoc.* 164: 277–283.
- CAST, 1976, Application of sewage sludge to cropland: Appraisal of potential hazards of the heavy metals to plants and animals, Council for Agricultural Science and Technology, Report 64, Ames, IA.
- CAST, 1980, Effects of sewage sludge on the cadmium and zinc content of crops, Council for Agricultural Science and Technology, Report No. 83, Ames, IA.
- CDC, 1991, Preventing lead poisoning in young children: A statement by the Centers for Disease Control, U.S. Department of Health and Human Services, Atlanta, GA.
- Chaney, R.L., 1983, Potential effects of waste constituents on the food chain, pp. 152–240, in J.F. Parr, P.B. Marsh and J.M. Kla (Eds.), *Land Treatment of Hazardous Wastes*, Noyes Data Corp., Park Ridge, NJ.
- Chaney, R.L., 1988a, Metal speciation and interactions among elements affect trace element transfer in agriculture and environmental food-chains, pp. 219–260, J.R. Kramer and H.E. Allen (Eds.), *Metal Speciation: Theory, Analysis and Application*, Lewis Publishers, Chelsea, MI.
- Chaney, R.L., 1988b, Effective utilization of sewage sludge on cropland in the United States and toxicological considerations for land application. *Proc. 2nd. International Symposium on Land Application of Sewage Sludge*, Tokyo, Japan, Association for the Utilization of Sewage Sludge.
- Chaney, R.L. and P.M. Giordano, 1977, Microelements as related to plant deficiencies and toxicities, pp. 234–279, L.F. Elliot and F.J. Stevenson (Eds.), *Soils for Management of Organic Wastes and Waste Waters*, American Society of Agronomy, Madison, WI.
- Chaney, R.L. and S.B. Hornick, 1978, Accumulation and effects of cadmium on crops, *Proc. First International Cadmium Conference*, Metals Bulletin Ltd., London, England, pp. 125–140.
- Chaney, R.L. and J.M. Ryan, 1993, Heavy metals and toxic organic pollutants in MSW composts: Research results on phytoavailability, bioavailability, fate, etc., H.A.J. Hoitink and H.M. Keener (Eds.), *Science and Engineering of Composting: Design, Environmental, Microbiological and Utilization Aspects*, Renaissance, Worthington, OH.
- Chaney, R.L. and J.A. Ryan, 1994, Risk based standards for arsenic, lead and cadmium in urban soils, pp. 1–130, G. Kreysa and J. Wiesner (Eds.), *Die Deutsche Bibliothek – CIP–Einheitsaufnahme*, DECHEMA, Frankfurt.

- Chaney, R.L., P.T. Hundemann, W.T. Palmer, R.J. Small, M.C. White and A.M. Decker, 1978, Plant accumulation of heavy metals and phytotoxicity resulting from utilization of sewage sludge and sludge compost on cropland, *Proc. National Conference on Composting Municipal Residues and Sludges*, Information Transfer, Inc., Rockville, MD, pp. 86–96.
- Chaney, R.L., J.A. Ryan and S.L. Brown, 1996, Development of the US–EPA limits for chromium in land–applied biosolids and applicability of these limits to tannery by–product derived fertilizers and other Cr–rich soil amendments, *Proc. Chromium Environmental Issues Workshop*, San Miniato, Italy.
- Chapman, H.D., 1966, Diagnostic criteria for plants and soils, Div. Agric. Sci., University of California, Riverside.
- Chesworth, W., 1991, Geochemistry of micronutrients, pp. 1–30, in J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, 2nd ed., Soil Science Society of America, Madison, WI.
- Connor, J.J. and H.T. Shacklette, 1975, Background geochemistry of some rocks, soils, plants and vegetables in the conterminous United States, U.S. Geological Survey, Washington, D.C.
- Corey, R.B., L.D. King, C. Lue–Hing, D.S. Fanning, J.J. Street, and J.M. Walker, 1987, Effects of sludge properties on accumulation of trace elements by crops, pp. 25–51, A.L. Page, T.J. Logan and J.A. Ryan (Eds.), *Land Application of Sludge — Food Chain Implications*, Lewis Publishers, Chelsea, MI.
- Cunningham, J.D., J.A. Ryan and D.R. Keeney, 1975, Phytotoxicity and metal uptake of metal added to soils as inorganic salts or in sewage sludge, *J. Environ. Qual.* 4: 460–462.
- Deuel, L.E. and A.P. Swoboda, 1972, Arsenic toxicity to cotton and soybeans, *J. Environ. Qual.* 1: 317–320.
- Dowdy, R.H. and W.E. Larson, 1975, The availability of sludge–borne metals to various vegetable crops, *J. Environ. Qual.* 4: 278–282.
- Dowdy, R.H., S.E. Clapp, D.R. Linden, W.E. Larson, T.R. Halbach and R.C. Polta, 1994, Twenty years of trace metal partitioning on the Rosemont sewage sludge watershed, C.E. Clapp, W.E. Larson and R.H. Dowdy (Eds.), *Sewage Sludge: Land Utilization and the Environment*, American Society of Agronomy, Madison, WI.
- Dudas, M.J. and S. Pawluk, 1980, Natural abundances and mineralogical partitioning of trace elements in selected Alberta soils, *Can. J. Soil Sci.* 60: 763–771.
- Elinder, C.–G., T. Kjellstrom, L. Friberg, B. Lind and L. Linnman, 1976, Cadmium in kidney cortex, liver and pancreas from Swedish autopsies, *Arch. Environ. Health* 31: 293–302.
- Elinder, C.–G., 1985, Cadmium: Uses, occurrence and intake, pp. 23–63, L. Friberg, C.–G. Elinder, T. Kjellstrom and G.F. Nordberg (Eds.), *Cadmium and Health: A Toxicological and Epidemiological Appraisal*, Vol. I, CRC, Boca Raton, FL.
- Elrashidi, M.A., D.C. Adriano and W.L. Lindsay, 1989, Solubility, speciation and transformations of selenium in soils, pp. 51–63, in L.W. Jacobs (Ed.), *Selenium in Agriculture and the Environment*, American Society of Agronomy, Madison, WI.
- Epstein, E., 1997, *The Science of Composting*, Technomic, Lancaster, PA.
- Evans, H.J., E.R. Puris and F.E. Bear, 1950, Molybdenum nutrition of alfalfa, *Plant Physiol.* 25: 555–566.
- Fasset, D.W., 1975, Cadmium: Biological effects and occurrence in the environment. *Am. Rev. Pharmacol.* 15: 425–535.

- Flanagan, P.R., J.S. McLellan, J. Haist, M.G. Cherian, M.J. Chamberlain, and L.S. Valberg, 1978, Increased dietary cadmium absorption in mice and human subjects with iron deficiency, *Gastroenterology* 74: 841–846.
- Fox, M.R.S., 1988, Nutritional factors that may influence bioavailability of cadmium, *J. Environ. Qual.* 17: 175–180.
- Friberg, L. and J. Vostal. 1972, *Mercury in the Environment*, CRC, Cleveland, OH.
- Friberg, L., C.–G. Elinder, T. Kjellstrom and G.F. Nordberg, 1974, *Cadmium and Health: A Toxicological and Epidemiological Appraisal*, Vol. I, *Exposure Dose and Metabolism*, CRC, Boca Raton, FL.
- Friberg, L., C.–G. Elinder, T. Kjellstrom and G.F. Nordberg, 1974, *Cadmium and Health: A Toxicological and Epidemiological Appraisal*, Vol. II, *Effects and Response*, CRC, Boca Raton, FL.
- Friberg, L., M. Piscator, G. Nordberg, and T. Kjellstrom, 1974, 248. *Cadmium in the Environment*, 2nd ed., CRC, Cleveland, OH.
- Gerloff, G. C., P.R. Stout and L.P. Jones, 1959, Molybdenum–manganese–iron antagonisms in the nutrition of tomato plants, *Plant Physiol.* 34: 608–613.
- Gough, L.P., H.T. Shacklette, and A.A. Case, 1979, Element concentrations toxic to plants, animals and man, U.S. Department of Interior, Geological Survey, *Geological Survey Bulletin*, 1466, Washington, D.C.
- Grace, N.D. and P.L. Martinson, 1985, The distribution of Mo between the liver and other organs and tissues and live weight gains of grazing sheep, pp. 534–536, C.F. Mills et al. (Eds.), *Trace Elements in Man and Animals* TEMA 5, Commonwealth Agric. Bureaux, Farnham Royal, England.
- Gupta, U.C., E.W. Chipman and D.C. Mackay, 1978, Effects of molybdenum and lime on the yield and molybdenum concentration of vegetable crops grown on acid sphagnum peat soil, *Can. J. Plant Sci.* 58: 983–992.
- Hambridge, K.M., C. Hambridge, M. Jacobs, and J.D. Baum, 1972, Low levels of zinc in hair, anorexia, poor growth and hypogeusia in children, *Pediatr. Res.* 6: 868–874.
- Hambridge, K.M., C.W. Casey and N.F. Krebs, 1987, Zinc, pp. 1–137, W. Mertz (Ed.), *Trace Elements in Human and Animal Nutrition*, Vol. 2, Academic Press, New York.
- Hansen, J.C., H.C. Wulf, N. Kormann, and K. Alboge, 1985, Cadmium concentration in blood samples from an East Greenlandic population, *Danish Med. Bull.* 32: 277–279.
- Harrison, R.M. and M.B. Chirgawi, 1989, The assessment of air and soil contributors of some trace metals to vegetable plants: II. Translocation of atmospheric and laboratory generated cadmium aerosols to and within vegetable plots, *Sci. Total Environ.* 83: 35–45.
- Harter, R.D., 1991, Micronutrient adsorption–desorption reactions in soils, pp. 59–87, in J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI.
- Haygarth, P.M., A.F. Harrison, and K.C. Jones, 1995, Plant selenium from soil and the atmosphere, *J. Environ. Qual.* 24: 768–771.
- Holmgren, G.G.S., M.W. Meyer, R.L. Chaney, and R.B. Daniels, 1993, Cadmium, lead, zinc, copper and nickel in agricultural soils of the United States of America, *J. Environ. Qual.* 22: 335–348.
- Hovmand, M.F., J.C. Tjell and H. Mosbaek, 1983, Plant uptake of airborne cadmium, *Environ. Pollut. Ser. A.* 30: 27–38.
- Jacobs, L.W., D.R. Keeney, and L.M. Walsh, 1970, Arsenic residue toxicity to vegetable crops grown on plainfield sand, *Agron. J.* 62: 588–591.
- Johnson, W.R. and Proctor, J, 1977, A comparative study of metal levels in plants from two contrasting lead–mine sites, *Plant Soil* 46: 251–257.

- Jones, J.B., 1991, Plant tissue analysis in micronutrients, pp. 477–521, J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI.
- Kagi, J.H.R. and B.L. Vallee, 1960, Metallothionein: A cadmium and zinc-containing protein from equine renal cortex, *J. Biol. Chem.* 235: 3460.
- Kolonel, L.N., 1976, Association of cadmium with renal cancer, *Cancer*, 37: 1782–1787.
- Krauskopf, K.B., 1967, *Introduction to Geochemistry*, McGraw–Hill, New York.
- Kubota, J., 1977, Molybdenum status of United States soils and plants, W.R. Chappel and K.K. Peterson (Eds.), *Molybdenum in the Environment*, Vol. 2, Marcel Dekker, New York.
- Kubota, J., V.A. Lazar, L.N. Langan and K.C. Beeson, 1961, The relationship of soils to molybdenum toxicity in cattle in Nevada, *Soil Sci. Soc. Am. Proc.* 25: 227–232.
- Kubota, J., V.A. Lazar, G.H. Simonson and W.W. Hill, 1967, The relationship of soils to molybdenum toxicity in grazing animals in Oregon, *Soil Sci. Soc. Am. Proc.* 31: 667–671.
- Lee, K.W. and D.R. Keeney, 1975, Cadmium and zinc additions to Wisconsin soils by commercial fertilizers and wastewater sludge application, *Water, Air, Soil Pollut.* 5: 109–112.
- Levender, O.A., 1979, Lead toxicity and nutritional deficiencies, *Environ. Health Perspect.* 29: 115–125.
- Levy, L.S., F.J.C. Roe, D. Malcom, G. Kazanatzis, J. Clark, and H.S. Platt, 1973, Absence of prostatic changes in rats exposed to cadmium, *Ann. Occup. Hyg.* 16: 111–118.
- Logan, T.J. and R.L. Chaney, 1983, Utilization of municipal wastewater and sludges on land–metals, Workshop on Utilization of Municipal Wastewater and Sludge on Land, Denver, CO.
- Logan, T.J., A.C. Chang, A.L. Page and T.J. Ganje, 1987, Accumulation of selenium in crops grown on sludge-treated soil, *J. Environ. Qual.* 16(4): 349–352.
- Lucas, P.A., A.G. Jariwalla, J.H. Jones, J. Gough and P.T. Vole, 1980, Fatal cadmium fume inhalation, *Lancet* 2: 205.
- Lue–Hing, C., R.I. Pietz, P. Tata, R. Johnson, R. Sustich and T.C. Granato, 1999, A national sewage sludge survey: Quality status relative to the part 503 Rule, WEFTEC '99, New Orleans, Louisiana, Water Environment Federation, Arlington, VA.
- Lund, L.J., E.E. Betty, A.L. Page and R.A. Elliott, 1981, Occurrence of naturally high cadmium levels in soils and its accumulation by vegetation, *J. Environ. Qual.* 10: 551–556.
- Ma, L.Q., F. Tan and W.G. Harris, 1997, Concentration and distribution of eleven metals in Florida soils, *J. Environ. Qual.* 26: 769–775.
- Mahaffey, K.R. and J.E. Vanderveen, 1979, Nutrient–toxicant interactions: Susceptible populations, *Environ. Health Perspect.* 29: 81–87.
- Malcom, D., 1972, Potential carcinogenic effect of cadmium in animals and man, *Ann. Occup. Hyg.* 15: 33–37.
- Marston, H.R., 1950, Problems associated with copper deficiency in ruminants, W.D. McElroy and B. Glass (Eds.), *Copper Metabolism Symposium on Animal, Plant and Soil Relationships*, Johns Hopkins University Press, Baltimore, MD.
- Mayland, H.F., L.F. James, K E. Panter and J.L. Sonderegger, 1989, Selenium in seleniferous environments, 15–50. L.W. Jacobs (Ed.), *Selenium in Agriculture and the Environment*, American Society of Agronomy, Soil Science Society of America, Madison, WI.
- McBride, M.B., 1995, Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective?, *J. Environ. Qual.* 24: 5–18.

- McKenzie-Parnell, J.M., and G. Eyon, 1987, Effect of New Zealand adults consuming large amounts of cadmium in oysters, pp. 420–430, D.D. Hemphill (Ed.), *Trace Substances in Environmental Health—XXI, Proc. of the University of Missouri's 21st Annual Conference on Trace Substances in Environmental Health*, St. Louis, MO.
- McKenzie-Parnell, J.M., T.E. Kjellstrom, R.P. Shaarma and M.F. Robinson, 1988, Unusually high intake and fecal output of cadmium and fecal output of other trace elements in New Zealand adults consuming dredge oysters, *Environ. Res.* 46: 1–14.
- McLaughlin, M.J., L.T. Palmer, K.G. Tiller, T.A. Beech and M.K. Smart, 1994, Increased soil salinity causes elevated cadmium concentrations in field-grown potato tubers, *J. Environ. Qual.* 23: 1013–1018.
- McNeal, J.M. and L.S. Balistrieri, 1989, Geochemistry and occurrence of selenium: An overview, pp. 1–13, in L.W. Jacobs (Ed.), *Selenium in Agriculture and the Environment*, American Society of Agronomy, Madison, WI.
- Mermut, A.R., J.C. Jain, L. Sog, R. Kerrich, L. Kozak and S. Jana, 1996, Trace element concentrations of selected soils and fertilizers in Saskatchewan, *J. Environ. Qual.* 25: 845–853.
- Mertz, W., 1967, The role of chromium in glucose metabolism, D.D. Hemphill (Ed.), *Trace Substances in Environmental Health — I. University of Missouri Annual Conf., 1st Proc.*, University of Missouri.
- Miller, E.R., L. Xingen, and D.E. Ullrey, 1991, Trace elements in animal nutrition, pp. 593–662, J.J. Mortvedt, F.R. Cox, L.M. Schuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI.
- Millner, J.E., J.J. Hassett, and D.E. Koeppe, 1976, Uptake of cadmium by soybeans as influenced by soil cation exchange capacity, pH and available phosphorus, *J. Environ. Qual.* 5: 157–160.
- Mills, C.F. and G.K. Davis, 1987, Molybdenum, pp. 429–463, W. Mertz (Ed.), *Trace Elements in Human and Animal Nutrition*, Vol.1, 5th ed., Academic Press, San Diego, CA.
- Moraghan, J.T. and H.J. Mascagni, Jr., 1991, Environmental and soil factors affecting micronutrient deficiencies and toxicities, *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI.
- Mortvedt, J.J., D.A. Mays and G. Osborn, 1981, Uptake by wheat of cadmium and other heavy metal contaminants in phosphate fertilizers, *J. Environ. Qual.* 10: 193–197.
- Mortvedt, J.J., F.R. Cox, L.M. Shuman, and R.M. Welch, 1991, *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI.
- Moss, L.H., E. Epstein and T. Logan, 2002, Comparing the characteristics, risk and benefits of soil, amendments and fertilizers used in agriculture. 16th Annual Residuals and Biosolids Management Conference — Privatization, Innovation and Optimization: How to Do More for Less, Austin, Texas, Water Environment Federation, Alexandria, VA.
- NRC, 1974, Chromium, National Research Council, 155. National Academy of Sciences, Washington, D.C.
- NRC, 1980, Mineral Tolerance of Domestic Animals, National Research Council, National Academy of Sciences, Washington, D.C.
- Nielsen, F.H., 1984, Ultratrace elements in nutrition, *Annu. Rev. Nutr.* 4: 21–41.
- Olsen, S.R. and F.W. Watanabe, 1979, Interaction of added gypsum in alkaline soils with uptake of iron, molybdenum, manganese and zinc by sorghum, *Soil Sci. Soc. Am. J.* 43: 125–130.
- Onken, B.M. and L.R. Hossner, 1995, Plant uptake and determination of arsenic species in soil solution under flooded conditions, *J. Environ. Qual.* 24: 373–381.

- Page, A.L., 1974, Fate and effects of trace elements in sewage sludge when applied to agricultural lands, Report No. EPA-670/2-74-005. U.S. Environmental Protection Agency, Washington, D.C.
- Page, A.L., F.T. Bingham, and A.C. Shang, 1981, Cadmium, pp. 77-109, N.W. Lepp (Ed.), *Effect of Heavy Metal Pollution on Plants*, Vol. 1. Applied Science, Barking, Essex, England.
- Pais, I. and J. Jones, J.B., 1997, *The Handbook of Trace Elements*, St. Lucie Press, Boca Raton, FL.
- Parr, J.F., E. Epstein, R.L. Chaney and G.B. Willson, 1977, Impact of the disposal of heavy metals in residues on land and crops, pp. 126-133, *Proc. 1977 National Conference on Treatment and Disposal of Industrial Wastewaters and Residues*, Houston, Texas. Information Transfer, Rockville, MD.
- Payne, C.G., 1977, Involvement of molybdenum in feather growth, *Br. Poult. Sci.* 18: 427-432.
- Pierce, F.J., H. Dowdy and D.F. Grigal, 1982, Concentrations of six trace metals in some major Minnesota soil series, *J. Environ. Qual.* 22: 805-811.
- Prasad, A.D., A. Miale, Jr., A. Farid, H.H. Sandstead and R. Schuler, 1963, Zinc metabolism in patients with the syndrome of iron deficiency anemia, hepatosplenomegaly, dwarfism and hypogonadism, *J. Lab. Clin. Med.* 61: 537-549.
- Pulido, P., J.H.R. Kagi, and B.L. Vallee, 1966, Isolation and some properties of human metallothionein, *Biochemistry* 5: 1768.
- Ryan, J.A., H.R. Pahren, and J.B. Lucas, 1982, Controlling cadmium in the human food chain: A review and rationale based on health effects, *Environ. Res.* 28: 251-302.
- Reddy, J., D. Svoboda, D. Azarnoff, and R. Dowas, 1973, Cadmium induced Leydig cell tumors of rat testis: Morphologic and cytochemical study, *J. Nat. Cancer Inst.* 51: 891-903.
- Römhelt, V. and H. Marschner, 1991, Function of micronutrients in plants, 297-328, J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, 2nd ed., Soil Science Society of America, Madison, WI.
- Scheinberg, H.I., 1969, The essentiality and toxicity of copper in man, *Trace Substances in Environmental Health - III. Annu. Conf. 3rd. Proc.* University of Missouri, Columbia.
- Schnitzer, M., 1978, Humic substances, M. Schnitzer and S.U. Kaha (Eds.), *Soil Organic Matter*, Elsevier, New York.
- Selby, L.A., A.A. Case, C.R. Dorn, and D.J. Wagstaff, 1974, Public health hazards associated with arsenic poisoning in cattle, *J. Am. Vet. Med. Assoc.* 165: 1010-1014.
- Shacklette, H.T., 1960, Soil and plant sampling at the Mahoney Creek lead-zinc deposit, Revillagigedo Island, Southeastern Alaska, U.S. Geological Survey Prof. Paper 400-B, U.S. Geological Survey, Washington, D.C.
- Shacklette, H.T., 1970, Mercury content of plants, U.S. Geological Survey, Washington, D.C.
- Shaikh, Z.A. and J.C. Smith, 1980, Metabolism of orally ingested cadmium in humans, p. 569, B. Holmstedt, R. Lauwerys, M. Mercer and M. Rocker (Eds.), *Mechanism of Toxicity and Hazard Evaluation*, Elsevier, Amsterdam.
- Sharma, R.P., T. Kjellstrom and J.M. McKenzie, 1983, Cadmium in blood and urine among smokers and nonsmokers with high cadmium uptake via food, *Toxicology* 29: 163-171.
- Sherlock, J.C., 1984, Cadmium in foods and diet, *Experientia*. 40: 152-156.
- Shuman, L.M., 1991, Chemical forms of micronutrients in soil, pp. 113-144, J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, 2nd ed., Soil Science Society of America, Madison, WI.
- Staker, E.V. and R.W. Cummings, 1941, The influence of zinc on the productivity of certain New York peat soils, *Soil Sci. Soc. Am. Proc.* 6: 207-214.

- Stevens, D.R., L.M. Walsh, and D.R. Keeney, 1972, Arsenic phytotoxicity on Plainfield soil as affected by ferric sulfate or aluminum sulfate, *J. Environ. Qual.* 1: 301–303.
- Sunderman, F.W.J., 1971, Metal carcinogenesis in experimental animals, *Food Cosmet. Toxicol.* 9: 105–120.
- Sunderman, F.W.J., 1978, Carcinogenic effect of metals, *Fed. Proc.* 37: 40–46.
- Swaine, D.J., 1955, The trace element content of soils, *Brit. Soil Sci.* 48: 1–157.
- Toepfer, E.W., W. Mertz, M.M. Polansky, E.E. Roginski and W.R. Wolf, 1977, Preparation of chromium-containing material of glucose tolerance factor activity from brewer's yeast extracts and by synthesis, *J. Agr. Food Chem.* 25: 162–166.
- Tsutsumi, M., 1981, Arsenic pollution of arable land, pp. 181–182, K. Kitagishi and I. Yamane (Eds.), *Heavy Metal Pollution in Soils of Japan*, Japan Soil Science Press, Tokyo.
- Underwood, E.J., 1977, *Trace Elements in Human and Animal Nutrition*, 4th ed., Academic Press, New York.
- Underwood, E.J., 1981, *The Mineral Nutrition of Livestock*, 2nd ed., Commonwealth Agriculture Bureaux, Slough, England.
- U.S. Department of Agriculture, 1968, Summary of registered agricultural pesticide chemical uses, U.S. Department of Agriculture, Pesticide Regulation Division, Looseleaf N.P. Washington, D.C.
- USEPA, 1990, National sewage sludge survey: Availability of information and data and anticipated impacts on proposed regulations: Proposed Rule 40 CFR Part 503, *Fed. Reg.* 55: 47210–47283.
- Van Campen, D.R., 1991, Trace elements in human nutrition, pp. 663–701, J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI.
- Water Environment Association of Ontario, 2001, Fate and significance of selected contaminants in sewage biosolids applied to agricultural land through literature review and consultation with stakeholder groups, Water Environment Association of Ontario, Toronto.
- Webber, M.D. and J. Nichols, 1995, Organic and metal contaminants in Canadian municipal sludges and sludge compost, Wastewater Technology Centre, Burlington, Ontario.
- Welch, R.M., W.H. Allaway, W.A. House and Kubota, 1991, Geographic distribution of trace element problems, pp. 31–57, J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.), *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI.
- Wells, B.R. and J.I. Gilmore, 1977, Sterility in rice cultivars as influenced by MSMA rate and water management, *Agron. J.* 69: 451–454.
- WHO, 1982, Assessment of human exposure to cadmium and lead through biological monitoring, World Health Organization. Report EFP/82–26, Geneva, Switzerland.
- WHO, 1990, Environmental health criteria 101: Methylmercury, World Health Organization, Geneva, Switzerland.
- Woolson, E.A., 1983, Emissions, cycling and effects of arsenic in soil ecosystems, B.A. Fowler (Ed.), *Biological and Environmental Effects of Arsenic*, Elsevier Science, New York.
- Woolson, E.A., J.H. Axley and P.C. Kearney, 1971, The chemistry and phytotoxicity of arsenic in soils: I. Contaminated field soils, *Soil Sci. Soc. Am. Proc.* 35: 938–943.
- Yamagata, N. and I. Shigematsu, 1970, Cadmium pollution in perspective, *Bull. Inst. Public Health* 19: 1–27.
- Yang, S.P., M.M. Luo and H.J. Wei, 1985, Effect of molybdenum and tungsten on carcinogenesis, 160–161, in C.F. Mills et al. (Eds.), *Trace Elements in Man and Animals*, TEMA 5, Commonwealth Agriculture Bureaux, Farnham Royal, England.